

Phosphorus K-XANES Spectroscopy of P Adsorbed on Iron and Aluminum Oxide Minerals

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Introduction: Phosphorus enrichment of many cultivated soils following long-term inputs of P fertilizers has been pointed as a major cause of nonpoint source pollution of water bodies in agricultural watersheds. Although P is strongly retained by Al and Fe oxide minerals in non-calcareous soils, excessive P contents lead to an increase of P solubility, which may result in an increased P mobility. A better understanding of the surface configuration of adsorbed P on Al and Fe oxide minerals would help predict the affinity of P binding and its impact on soil P sorption capacity as the soil gets loaded with P. The objective of this study was to determine whether phosphorus K-XANES analysis reveals differences in the surface speciation of phosphate adsorbed on Fe and Al oxide minerals over a range of P concentrations, and at constant pH.

Methods and Materials: Phosphorus K-XANES analyses were performed at Beamline X-19A on samples containing phosphate adsorbed on goethite at levels between 10 and 480 mmol P/kg goethite (0.08 to 3.7 mmol/m²) at pH 6. A sample of gibbsite with phosphate adsorbed at near-maximum capacity (12 mmol/kg or 1.3 mmol/m²) at pH 6 was also analyzed. Data were collected in fluorescence mode at ambient temperature using a He flight path, a PIPS detector, and a Ge(111) monochromator.

Results: Related figures and a more detailed discussion of the results are presented in the Science Highlight section of the 2000 NSLS Activity Report. Phosphorus K-XANES spectra for phosphate adsorbed on gibbsite and goethite showed different features. However, regardless of whether the adsorbent was goethite or gibbsite, a shoulder on the high-energy side of the white-line peak was apparent at low level of adsorbed P (10 or 12 mmol/kg). For a range of adsorbed PO₄ concentrations on goethite, the prominence of the shoulder on the high-energy side of the white-line peak diminished systematically with increasing levels of adsorbed PO₄. The white-line peak intensity increased between 10, 20, and 480 mmol P/kg, but was constant for levels between 20 and 120 mmol P/kg goethite. The spectral changes indicated that there were multiple species of phosphate associated with the goethite surface at pH 6, depending on level of adsorbed PO₄.

Conclusions: In view of other infrared spectroscopic studies^{1,2}, the results suggest that bidentate phosphate species would be dominant at low levels of phosphate adsorption, and monodentate species (or other surface species) would occur at higher levels of adsorption.

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References: ¹R. L. Parfitt, A. R. Fraser, J. D. Russell, and V. C. Farmer, "Adsorption on Hydrous Oxides II. Oxalate, Benzoate, and Phosphate on Gibbsite," *Journal of Soil Science*, **28**, 40, 1977; ²M. I. Tejedor-Tejedor and M. A. Anderson, "Protonation of Phosphate on the Surface of Goethite as Studied by CIR-FTIR and Electrophoretic Mobility," *Langmuir*, **6**, 602, 1990.